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ACIDIC PRECIPITATION IN ONTARIO STUDY

CHEMICAL, MICROBIOLOGICAL AND PHYSICAL INTERACTIONS OF ACIDIC PRECIPITATION WITHIN A LAKE AND ITS DRAINAGE BASIN

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ACIDIC PRECIPITATION IN ONTARIO STUDY

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CHEMICAL, MICROBIOLOGICAL AND PHYSICAL INTERACTIONS OF
ACIDIC PRECIPITATION WITHIN A LAKE AND ITS DRAINAGE BASIN

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APIOS Report
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Chemical, Microbiological and Physical Interactions of
Acidic Precipitation within a Lake and its Drainage Basin

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Introduction

The purpose of this paper is to describe the major chemical interactions occurring between rainfall, a watershed and its included lake. Attention will be focused particularly on the reactions of carbon, nitrogen and sulfur because of the key roles they play in chemical and biological processes determining the pH of soils and lake waters. As this is part of a study concerning lake acidification due to acid precipitation in southern Ontario, Canada, emphasis is directed toward understanding the mechanism of acidification in Canadian Shield lakes. There are literally thousands of these lakes in the region and as many are situated on sparingly soluble granitic bedrock, they are very dilute and have little buffering capacity. In many lakes the pH is thought to be dropping rapidly and acid precipitation, currently of uncertain origin, appears to be the cause (Dillon et al. 1978). At the present rate of acid input, it is predicted that many Shield lakes could become acidic in less than 10 years (Parrot 1979) and as a result, large scale kills of aquatic biota could be expected.

The destruction of this aquatic resource would deal a severe economic blow to Ontario because much of its tourism is based upon sport fishing in the region (Parrott 1979). In addition, many of these lakes are surrounded by summer cottages which were located there because of the clean water and good fishing. To a number of the Ontario summer residents, the killing of the fishery would be considered a disaster.

Such emotions have been transmitted to the Ontario provincial and the Canadian federal governments and as a result lake acidification is presently considered the greatest environmental problem in Canada. Major funding has been made available to study the problem and this paper forms part of the effort being made to understand the mechanism of lake acidification.

Lake acidification is not new to Canada; a good example of the effect of acid fallout already exists in the region surrounding Sudbury, Ontario, the site of a nickel smelter that is the world's largest point source of SO_2 (Summers and Whelpdale 1976). Further oxidation of SO_2 in the atmosphere has produced sulfuric acid and caused lakes as far as 130 km from the site to become severely acidified (Conroy et al. 1975).

In Sweden and Norway, studies begun in about 1970 indicate that a widespread acidification of lakes is already occurring there. Mineral acid precursors, evidently produced mainly in Britain and the European industrial heartlands, are injected into the atmosphere, converted to sulfuric, nitric and hydrochloric acids, and then carried by prevailing winds across Norway and Sweden where they finally deposit with precipitation and dryfall. As both of these countries have numerous lakes situated on Precambrian Shield bedrock similar to that in Canada, the waters are generally poorly buffered and easily affected by incoming

acids (Oden 1976). The drop in pH in such lakes has been well documented and the failure of fisheries is becoming a frequent occurrence (Almer 1974, Dickson et al. 1975). In the northeastern United States acid rainfall has also been implicated in the lowering of pH and the disappearance of fish from many dilute lakes of the Adirondack Mountains of New York (Likens 1976).

The experiences of Norway, Sweden and the U.S.A. appear to be models for what is happening in Canada: rapid acidification of Canadian Shield lakes might well occur due to long range transport of acids. Evidence presently available supports this view (Dillon et al. 1978).

The Chemical Composition of Rainwater

Distilled water, when in equilibrium with CO_2 in the atmosphere, exhibits a slightly acid pH of about 5.6 . Rain water is the result of evaporation, essentially a distillation process, and therefore the pH of 'pure' rain water should be about 5.6 . In reality, however, the pH varies considerably, both temporally and regionally.

Rainfall in the southwestern U.S. tends to be neutral because of elevated concentrations of Ca, Mg, Na and K which are probably scavenged from air born dusts originating from the arid soils of the region (Gorham 1976, Fisher et al.

1968). The water is considerably more alkaline than if it were pure. In the eastern U.S. the rain is usually below pH 5 and is significantly more acid than distilled water. The cause of the acidity is elevated concentrations of mineral acids such as H_2SO_4 , HNO_3 and HCl , listed in order of importance (Cogbill and Likens 1974). The most acidic rains occur in the northeast where average annual pH can approach 4 in certain areas (Likens 1976). The burning of fossil fuels by heavy industry is thought to be the primary source of the acids (Likens 1976).

In Canada, precipitation monitoring stations, operated to obtain information on water chemistry, have been few in number in the past and therefore data describing the pH of rainfall across the country are lacking (Summers and Whelpdale 1976). The Experimental Lakes Area in northwestern Ontario (Schindler et al. 1976) shows annual average pH values of 4.9 - 5.0 for rain falling in 1970 and 1973 upon this unpopulated Precambrian Shield region. In Nova Scotia Herman and Gorham (1957) found the pH of precipitation to average 5.7 in a 2 year period in 1952 - 1954. A recent summary of data obtained in 1973 - 1977 (Dillon et al. 1978) based upon 25 precipitation monitoring sites and covering a mostly shield area of about 50,000 km² to the east and north of Georgian Bay, indicate a mean annual pH range of about 4.0 to 4.2. These low pH values are similar to those observed by Likens et al. (1972) at Hubbard Brook in the northeastern U.S.

Data of Likens et al. (1976) show the average ionic

composition of rainwater falling upon the Hubbard Brook Experimental Forest in New Hampshire from 1963 - 1974 (Tab.1). They argue that the overall balance of charge indicates no major ionic constituents were missed and that the data describe a dilute acid solution of H_2SO_4 and HNO_3 with some contaminants. It is concluded that the acid rain of the region is due mainly to H_2SO_4 and secondarily to HNO_3 . In Norway (Schaug and Semb 1976, Wright and Hendriksen 1976) the evidence similarly suggests that H_2SO_4 is the major acidic component in rainfall. Canadian data also support this by showing a strong correlation between acidity and SO_4^{2-} concentration in rain falling upon the Precambrian Shield of south-central Ontario (Dillon et al.1978).

In the discussions which follow, precipitation with a pH below 5.6 shall be considered to contain an excess of H^+ ion due to the presence of sulfuric and secondarily, nitric acids.

Physiography of the Central Ontario Canadian Shield

In Canada, some regions being severely affected by acid precipitation lie on the Precambrian Shield of central Ontario. The southern edge of the shield lies in the Great Lakes-St. Lawrence Forest Region. It is a heavily forested area composed of mixed stands of Eastern White Pine, Red Pine, Eastern Hemlock and Yellow Birch with lesser associations of broad leaf species such as Sugar and Red Maple, Red Oak, Basswood and White Elm. Boreal species such as White, Red and Black Spruce, Balsam Fir, Jack Pine, Poplar and White Birch are inter mixed. The central and northern

shield of Ontario is in the Boreal Forest Region, with White and Black Spruce being the characteristic species while Tamarac, Balsam Fir and Jack Pine are common. Although primarily coniferous, there is a general admixture of deciduous trees such as White Birch and Poplar (Hosie 1975).

The forests often stand directly upon Precambrian Shield bedrock which is composed mostly of granite, granite gneiss, granite pegmatite and migmatite. A shallow overburden of till, often of little buffering capacity, covers the bedrock to various depths, usually less than 1 meter, and in many locations the bedrock is exposed (Dillon et al. 1978, Chapman 1975). The soils, where they exist, would be mainly classified as acid podzols (Clayton et al. 1977), such soils being common in North America (except central) between the latitudes of 40 - 60 degrees N. Typical soil pH would be 4.5 to 5.5, with still lower pH values being observed in well established evergreen forest soils (Strahler and Strahler 1973).

Podzols occur where the climate is sufficiently cold to slow bacterial degradative processes and where sufficient moisture exists to permit growth of larger green plants such as trees. A gradual buildup of plant litter on the forest floor gives rise to a thick surface mat of slowly decaying organic matter, a major characteristic of podzols, which tends to prevent dehydration of the under lying soil (Strahler and Strahler 1973). Figure 1 illustrates a typical podzol soil profile. The above authors indicate that humic acids, produced from the decaying plant litter, leach the

upper soil layers (L-H - Ah) of colloids and bases (eg. Ca, Mg and Na) as well as iron and aluminum oxides, leaving a characteristic ash grey Ae soil horizon composed largely of SiO_2 . Colloids, humus and iron oxides carried out of the Ae horizon accumulate in the B horizon, which may be dark in color, dense in structure, and in some cases, hardened to rocklike consistency.

To better understand the interaction between rain and a forest growing in a podzol, it will be instructive to analyse the various reactions occurring, starting with the rain striking the forest canopy.

Rainwater - Forest Canopy Interactions

In a 30 year old northern Ontario Jack Pine stand, considerable changes in the chemical composition of the rain occurred after contacting the leaves (Foster 1974). Table 2 shows the concentration of several elements in the rain, canopy throughfall and stemflow. Approximately 80 % of the rain reacted with the canopy to become throughfall and therefore it is clear that the forest exerts a large effect upon the composition of rain reaching the soil. The drop in pH is a notable feature. In spite of increased concentrations of cations in the throughfall, the H^+ ion concentration also rose. To ensure a balance of charge, significant quantities of anions such as SO_4^{2-} and Cl^- must have also been leached from the leaves by the throughfall and subsequently deposited on the soil. The HCO_3^- ion should not be important because it

would be present in extremely small concentrations at this pH.

Similar interactions between rain and forest canopy appear to take place in hardwood forests. Eaton et al. (1973) give data for the Hubbard Brook Experimental Forest wherein they describe the ionic composition of throughfall and precipitation falling in a stand of Sugar Maple, American Beech and Yellow Birch (Table 3). Where comparisons are possible, dramatic increases can be seen in all the ionic species, except H^+ ion, after rain has fallen through the canopy. The large increases in K^+ and SO_4^{2-} are notable. In the case of H^+ ion, the concentration dropped by a factor of 8.1. This is in striking contrast to the increase in H^+ , by a factor of 2.1, occurring in the Jack Pine throughfall.

Other data of Eaton et al. (1973) are of interest (Table 4). Both Na and S are removed from the leaves in quantities far above those actually contained within them when they are healthy and fully developed. This indicates that considerable 'pumping' of these elements must be occurring from the soil to the leaves. If elements are transported up the xylem of the trees at concentrations the same as that in the soil water, this 'pumping' might be easily explained: in order for the leaves to obtain enough of the most limiting nutrient, large excesses of other elements must also be transported up the length of the tree. These excess elements could either return to the root zone via the phloem or be beneficially leached by rainfall from the leaves and bark. Not all elements can return to the roots via the phloem

(Zeigler 1963) and therefore leaching may be an important process in removing surplus ions and thereby maintaining suitable solute concentrations.

In trees, this pumping mechanism is a passive response to transpiration: the more rapid the transpiration, the greater is the flow of water and solutes up the xylem from the soil (Leopold and Kriedemann 1975). The rate at which transpiration, and hence nutrient flow, occurs depends upon the species of plant. For example, the stems of deciduous trees have higher xylem sap conductivities than do conifers ($1.6 - 3$ vs. $0.6 \text{ cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$) (Leopold and Kriedemann 1975). Environmental conditions which alter the supply of water to the roots and the evaporation rate at the leaves are also of central importance in determining the rate of water uptake.

As water is transpired from the leaves, the concentration of solute molecules will rise in the leaves. A portion of the solute will be incorporated into plant tissue and a portion will return to the soil water via the phloem. The remaining solutes are leached from the leaves via the rainfall. Several mechanisms can be postulated to describe the loss of solute from the leaves.

First, if the mechanism is simply a mass transfer of water and solute from the leaves to the rain, the pH of the throughfall will be an average of the mixed solutions:

$$\text{i.e. } (H_c^+) = \frac{(H_l^+) * \text{Vol.}_l + (H_r^+) * \text{Vol.}_r}{\text{Vol.}_l + \text{Vol.}_r}$$

Where:

(H_l^+) = hydrogen ion concentration in leafwater awaiting transpiration

(H_r^+) = hydrogen ion concentration in rainwater

Vol._l = volume of leafwater leached into rain

Vol._r = volume of rainwater into which leafwater was leached

(H_c^+) = hydrogen ion concentration in combined solutions

This assumes that all the chemical species are completely dissociated.

A second mechanism could involve exchange reactions between rain and leafwaters. If, for example, H^+ ion in rain were exchanged for Ca^{2+} in leafwater, the (H^+) would decrease while that of the leafwater would increase. However, the rain (as throughfall) and the leafwater (returning to the soil via the phloem) would mix in the soil, the net effect on soil water pH being zero.

In neither of the above two mechanisms would the throughfall from trees have any net effect upon the hydrogen ion concentration of the soil.

Soils and Acidity

Canadian Shield Soils

The majority of the Canadian Shield is overlain with humo-ferric podzol (Clayton et al. 1977). Such podzols are naturally acidic and occur in forests, the most extreme examples being seen in coniferous forests such as those existing in the Canadian Shield (Foster 1969, Rogers and Adams 1966). A typical soil profile is described in Table 5 wherein the characteristic low pH is well evident, especially at the surface. The pH observed in a soil-water mixture would be slightly higher (perhaps 0.5 units) than is indicated here by the 0.1 M CaCl_2 extraction (Black 1968). In this example, the L-H horizon, which is the layer of decomposing organic matter, is not shown but it typically would be of similar acidity as the Ae horizon. The aluminum and iron have been largely leached out of the Ae horizon and accumulated in the Bfh horizon. The % base saturation is very low and indicates a high degree of Ca and Mg leaching from the upper soil profile.

An Overview of Natural Acidification in Soils

The causes of acidification in podzols appear to be as numerous and varied as are the authors who describe the process. The following is a partial sampling of the literature which deals with podzol acidification:

- 1) Foster (1969) and Rogers and Adams (1966) state that the production of acids is due to organic matter degradation but they give no mechanisms or references.

2) Strahler and Strahler (1973) state that coniferous trees "do not use large amounts of bases and hence do not restore them to the soil surface. The result is that humic acids, produced from the abundant plant litter and humus, leach the upper soil strongly of bases, colloids, and the oxides of iron and aluminum, leaving a characteristic ash-grey Ae horizon composed largely of silica". No references were cited.

3) Malmer and Nilsson (1974) suggest that H_2S or NH_4^+ oxidation and inorganic matter decomposition may cause the acidity, with the latter being more important. They further state "an increase in the amount of organic matter in the soil also results in a more acid reaction if the supply of metal cations does not increase at the same time to a corresponding degree. The acid reaction is brought about by an increase in the exchange capacity of the soil, and the increase gives rise to a decrease in the metal ion saturation (degree of neutralization). But in this case it is only the amount of organic matter that is important, as spruce needle litter is by itself relatively poor in bases, producing a much more acid reaction than most other vegetable litter". They cite no references.

4) Dickson (1975) writes that the uptake of cations by spruce and pine and the release of hydrogen ions and humic substances may acidify formerly arable land from pH 6 down to pH 4 in a few decades. He also acknowledges the possible acidifying effects of NH_4^+ and S^{2-} oxidation. He cites no papers.

5) Reuss (1975) describes a mechanism wherein plants usually take up more anion than cations but they contain less anions than cations because species such as NO_3^- and SO_4^{2-} are converted into protein. He indicates that the excess cations are balanced by organic ions formed in the plant, and that upon plant death, these basic salts of organic acids are hydrolyzed; "the bases are removed and leached as bicarbonates and the remaining litter is acidic due to the presence of these organic acids. If the pH lowers to the point that bicarbonates can no longer exist, this mechanism of leaching is no longer operative. Bases then can only leach in conjunction with the above anions or by chelation with certain organic complexes". He cited no references.

6) Coleman and Thomas (1967) state that soil acidity is controlled in large part by ion exchange and other adsorptive reactions. They indicate that layered silicates and oxide minerals, as well as organic matter, influence the acid properties of soils. Actual acid production is attributed to oxidation of ammonium fertilizers and FeS and to organic acids released from plant material, both live and decaying. They indicate that organic acids may be especially important in podzols and cite Mortensen (1963) and Mortensen and Himes (1964) to back up this point. A careful examination of these two papers, however, fails to substantiate their statement. A further survey of the soil literature by the present author was unsuccessful in finding data which would show that organic acids were responsible

for permanent soil acidity.

Some or all of the above theories on soil acidification may be valid. It is clear, however, that a unified view on the acidification of podzols does not presently exist.

Soil Acidity According to C.A. Black

A simple, but elegant explanation of the soil acidification process can be found in "Soil-Plant Relationships" (Black 1968). Although this description is not specifically addressed to processes in forest soils, it would still appear to be pertinent.

a) Acidity and CO_2 . Black's first observation is that the concentration of soluble salts in surface soils is inversely proportional to the amount of rainfall (Jenny and Leonard 1934)(Fig. 2). These data were obtained on the 11 degree C isotherm cutting east-west across the United States. The loss from the surface soil of soluble carbonates was strongly correlated to a surface soil decrease in pH (Fig. 3). If the soil were buffered only by the $\text{Ca}(\text{HCO}_3)_2$ - CaCO_3 system, the removal of all the calcium from the soil would presumably allow the H^+ ion concentration to reach pH 5.6 given a pCO_2 in the soil the same as that in air (0.0003 atm.). If the soil pCO_2 were greater due to plant and microbial respiration, a typical level being 0.002 - 0.01 atm. (Black 1968), the expected pH would be in the range 5.25 - 4.9 (Stumm and Morgan 1970). Thus an acidic soil can be produced by CO_2 alone, provided the soil was initially poor in buffering material. It should be noted that significant

portions of the Canadian Shield in eastern Canada are overlain with podzols which contain very little CaCO_3 (Dillon et al. 1977) and are poorly buffered, and it is conceivable that at least part of their acidity is attributable to soil CO_2 .

b) Ammonia Nitrification. Black's second observation concerned the work of Desai and Subbiah (1951) in which they added various amounts of organic and inorganic fertilizers to moist soils. After an incubation period they found that water soluble calcium, magnesium and potassium were released in quantities proportional to the amount of NO_3^- - nitrogen formed. This indicated that nitric acid had been produced from the ammonia fertilizer (nitrified) and that this acid reacted with the base containing minerals to produce the soluble cations. No correlation was found between the oxidized carbon and the cations made soluble and from this it might be concluded that microbial production of organic acids was not an important process in the soil acidification. This is not surprising when one considers that the relatively strong organic acids, such as acetic and formic, which would be most active in dissolving minerals, will probably have a short lifetime in most soils. Evidence for a short lifetime is seen in the very low concentrations of these acids in natural lake waters (Wetzel 1975, p. 566).

Although the relative importance of strong mineral acid production in a particular soil may not be agreed upon by various workers, the production of such acids appears to be

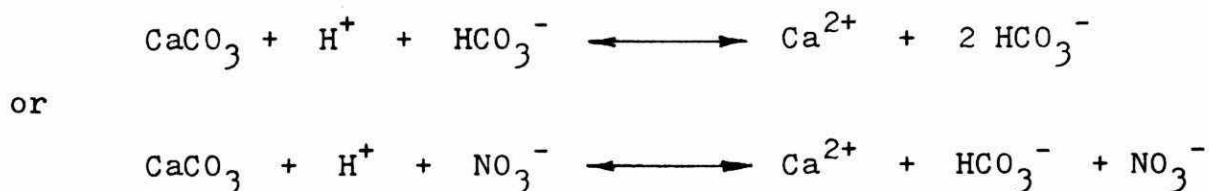
generally acknowledged (Malmer and Nilsson 1974, Dickson 1975, Russell 1961). Black states that the nitrification of ammonia in 1 mole of ammonium nitrate fertilizer produces 2 moles of nitric acid, while the nitrification of 1 mole of ammonium sulfate yields 2 moles of nitric acid and 1 mole of sulfuric acid. He indicates that even the base ammonium hydroxide results in 1 mole of nitric acid upon nitrification. An example of soil acidification by this mechanism is given by Pierre (1927) in Table 6. Soil pH values as low as 4.2 have been observed on tea plantations which have received longterm applications of $(\text{NH}_4)_2\text{SO}_4$ (Russell 1961).

From the forgoing, it appears that mineral acid production from fertilizers is an important mechanism in the acidification of agricultural soils. The same mechanism may be operating on forest soils, but in this case the ammonia is supplied via precipitation, not by fertilizer applications. In the relatively unpolluted environment of the Experimental Lakes Area of northwestern Ontario, the ammonia input from precipitation is about 21 ueq.L^{-1} (Schindler et al. 1976) which upon nitrification would supply 42 ueq.L^{-1} of H^+ . This H^+ ion concentration is equivalent to that expected in rainwater of pH 4.4. Thus, in a poorly buffered Canadian Shield soil one might expect to observe an acid pH which was caused by nitrification of ammonia delivered in precipitation.

The Fate of Acids in Humo-Ferric Podzols

A knowledge of the fate of acids which impinge upon Shield soils is required if we are to properly evaluate the effects of acid rain. Some valuable information can be gained by studying the path of acids such as nitric and carbonic which are naturally produced in soils not subject to anthropogenic acid precipitation. Although many soil types are present in the Shield, we have limited our discussion here to the Humo-Ferric podzol because it is the most common (Clayton et al. 1977).

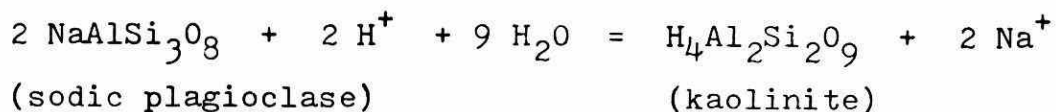
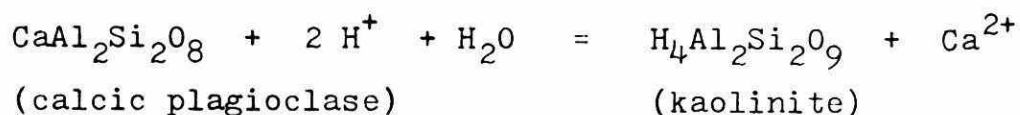
A glance at Table 5 reveals that pH increases from 3.3 at the soil surface to 5.1 at a depth of about 200 cm, a decrease by a factor of 63 in the H^+ concentration. If we assume that the acids do not volatilize, but instead pass down through the soil column dissolved in infiltration water, then some reaction must be occurring by which the H^+ ion is being consumed. In soils containing appreciable $CaCO_3$ the consumption mechanism would probably be:



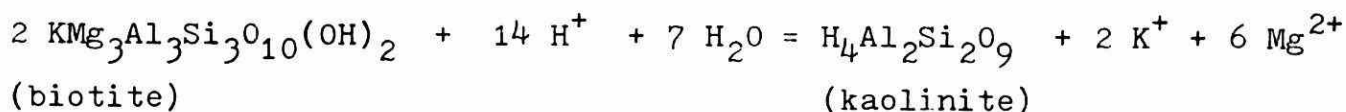
In the Humo-Ferric podzol of Table 5, the % base saturation reveals that most of the soluble cations have been leached from the A and B horizons and it is probable that the above, or similar reactions, were responsible for the leaching.

The result of such buffering reactions is that acid infiltration water is made more alkaline as it passes through the soil column.

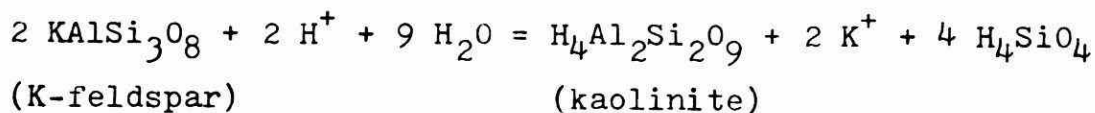
In Humo-Ferric podzols which are initially deficient in bases or which were depleted by leaching, pH may be buffered by dissolution of, or cation exchange with, the silicate minerals of the soils. One reaction that has been particularly well documented is the dissolution of plagioclase (Garrels and Mackenzie 1967) which can be roughly represented as:



Several other known reactions (roughly stated) are the slower dissolution of biotite:



and of K-feldspar:



The H^+ ion indicated in the equations might come from H_2CO_3 , HNO_3 or other natural sources or be of anthropogenic origin. It should be realized that the velocity of these reactions will directly affect how well these minerals perform as buffering agents. If the reaction rates are slow compared to the production of H^+ ion, then the solution will be acidic even though the potential buffering capacity may be large. Furthermore, when H^+ ion input is equal to H^+ ion consumption by the buffering agent, the pH of the solution could be quite low. Thus, it is conceivable that soil could be well buffered at a pH of 4.5, for example.

Garrels and Mackenzie (1967) present strong evidence that the forgoing reactions are important in the weathering of granite rock in the Sierra Nevada mountains and it is not unlikely that such weathering is occurring on the extensive granite formations of the Canadian Shield. It is unlikely, however, that weathering, and hence acid neutralization, will occur at a rate sufficient to significantly reduce the H^+ ion concentration in rain or soil water. If the granite bedrock were finely divided to sand size or smaller by physical weathering, the surface area over which chemical reaction could take place would be greatly increased and it is possible that such fine textured material would be reactive enough to significantly buffer acid solutions (Kramer 1976). Some evidence for this comes from Brunskill et al. (1971) who suggested that dissolution of finely divided aluminum silicate minerals (in order of abundance, quartz, plagioclase, K-feldspar, biotite and/or muscovite) contained in lake

sediments may control the pH in some calcium deficient, poorly buffered lakes on the northwestern Ontario Canadian Shield. In that region of Ontario the soils are essentially made up of glacial till of a similar mineralogic composition to that of the sediments and it seems reasonable to suggest that these soils may have considerable buffering capacity against acid. Lack of data, concerning the distribution of such mineral soils across the Canadian Shield, precludes us from estimating how geographically widespread such buffering activity might be (Kramer 1976).

The Leaching of Aluminum in Soils

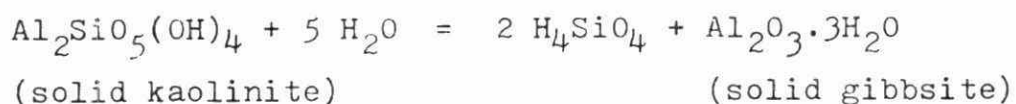
Lakes that are contained in watersheds subject to acidic precipitation have been known to exhibit elevated dissolved aluminum concentrations (Cronan and Schofield 1979). Aluminum can be toxic to plants and animals (Burrows 1977) and for this reason a brief discussion of aluminum behaviour in acid soils appears warranted.

A reexamination of Table 5 reveals that the surface Ae soil horizon of the humo-ferric podzol is largely depleted of aluminum. The aluminum concentrations indicate that this element has been leached from the upper horizon and subsequently accumulates in the Bfh and Bf horizons. The observation that dissolved aluminum concentrations are elevated in some acidified lakes suggests that the leaching of aluminum from soils and/or sediments may be partly controlled by pH. The following paragraph describes some further evidence which supports this

view.

Tamm and Wiklander (unpublished- cited by Malmer and Nilsson 1974) showed soils to release aluminum when irrigated with water containing H_2SO_4 . Coleman et al.(1959) show clearly how the quantity of exchangeable (potentially leachable) aluminum is a function of pH (Fig. 4), at least in their North Carolina acid soils. Each of the points on the graph represents a separate soil sample and the pH values are the H^+ ion concentrations of the soils when collected. One explanation for the increase in exchangeable aluminum at an acid pH may simply be that aluminum metal (probably in the polyhydroxide form) is more soluble in an acidic environment than in a neutral one. Magistad (1925) and Pierre et al. (1932), as cited in Black (1968), illustrate how aluminum solubility is a function of pH (Fig. 5 - solid line). They also show that the amount of aluminum in soil solution is strongly related to the soil pH. Thus, based solely upon the solubility of aluminum, one might reasonably predict that aluminum leaching from a soil or sediment would increase as the pH drops below pH 5.5 .

Several common aluminum containing minerals are also more soluble at acid pH than in neutral conditions. Kaolinite and gibbsite, which can interreact in the following way,



both exhibit minimum solubilities at about pH 6 (Stumm and Morgan 1970). As the pH drops below this value, the solubilities of both minerals increase dramatically (Fig. 6). From the solubility curves one would predict that aluminum would be leached from acid soils or sediments containing these minerals in a manner similar to that for aluminum polyhydroxides.

In light of the forgoing, the following hypothesis can be put forward. The loss of aluminum from upper soil horizons of the humo-ferric podzols is due to acid leaching, a process made possible by the low pH of the soil. As the acidic soil solution passes down through the soil column, it will be buffered by CaCO_3 , by reaction with other minerals such as plagioclase, or by reaction with organic material, either individually or in chorus. The result of the buffering action is that the solution becomes less acidic while proceeding downward in the soil profile and, in the B horizon, the pH will be high enough to allow the aluminum to precipitate from solution

According to Figures 4, 5 and 6, aluminum can be predicted not to leach in soils having a pH between 5.5 and 7. Referring to Table 5, it is observed that aluminum does not enter the C horizon but instead accumulates in the B horizon where the pH is 4.3 to 4.9 (CaCl_2). This is approximately equivalent to an aqueous pH of 4.8 - 5.4 and corresponds to a solubility minimum for aluminum. It appears that the data from the actual soil profile support the hypothesis that pH controls

leaching of aluminum.

Other Factors Affecting Soil Water Acidity

Soil Depth

The depth of soil covering the bedrock could well be an important factor in determining the buffer capacity of the soil. If the soil were only a few centimeters thick it is possible that insufficient time would be available for the acids to react with the mineral phase and therefore neutralization would be incomplete. As a result the soil solution would remain too acidic to allow precipitation of aluminum and thus both H^+ and aluminum ions would pass completely out of the soil and subsequently enter stream waters. This could account for some of the low pH values observed in some streams in the Shield (Jeffries et al. 1979, Bottomley 1974) and possibly explain the gradually dropping pH of some streams in Scandinavia (Oden and Ahl 1970); in these regions only a portion of the soils may be thick enough to neutralize the natural or anthropogenic acids present in the soil water. An extreme example of the effect of soil depth upon buffering would be the case where rain water contacted only exposed bedrock before entering a stream (i.e. zero soil depth). In the southern Ontario Shield such runoff would probably have the same pH as the rain, a value of about 4.

Permanent and Non-Permanent Acidity

In this study, acid content in soils has been attributed

to (1) high $p\text{CO}_2$ and hence carbonic acid and (2) mineral acids entering in precipitation or produced in the soil. Consideration of the effects of humic and fulvic acids has been omitted here for reasons described earlier in this paper in section 6 of "An overview of natural acidification of soils".

Soil waters which are acidic due to high $p\text{CO}_2$ should rapidly (minutes - hours) equilibrate with the atmosphere once in a stream and the pH should rise to 5.6 or above, depending upon the alkalinity. Alternatively, the pH of soil waters containing both carbonic and mineral acids would not rise as much upon atmospheric equilibration because of the permanent mineral acidity. This phenomenon will be important to workers measuring the pH of streams to determine if they are affected by acidic precipitation. In such cases it may be necessary to ensure that the samples are in equilibrium with air before the pH is taken.

Evaporation

The effects of evaporation, transpiration, and evapotranspiration upon solute concentration should be considered. The simplest example would be the concentrating of H_2SO_4 in soil water by evaporation. Using a four year average of data from the Experimental Lakes Area (Schindler et al. 1976), the evapotranspiration and storage was 66 % of precipitation i.e. the water volume was reduced by 2/3. If the average pH of the precipitation were 5, and the H^+ ion due mostly to non-volatile

H_2SO_4 , then the expected pH of the soil water would be 4.52 simply by evaporative concentration. This very simple mechanism appears to have been little discussed in the past but, theoretically at least, is of some importance.

Pulse Flows During Snowmelt

The high acidity seen in Spring runoff of the Norwegian and southern Ontario Shield watersheds requires some mention (Henriksen and Wright 1977 , Jeffries et al. 1979). These workers have shown that a large pulse of H^+ ion is added to streams during spring snowmelt and the pH of such waters can typically reach values of about 4.5 . It is thought that this acid pulse is due to overland flow of acid snowmelt water and that neutralization does not occur because no infiltration can take place while the ground is frozen. The lack of interaction with the soil evidently prevents buffering of the acid even in moderately well buffered watersheds. Jeffries et al.(1979) state that the littoral zones and tributaries of lakes in central Ontario are both spawning and nursery grounds for fish species such as lake trout (Salvelinus namaycush), brook trout (S. fontinalis), whitefish (Coregonus clupeaformis), and walleye (Stizostedion vitreum). They cite evidence that the salmonid larvae, at least, may be most sensitive to acid at this time of year. It is possible, therefore, that lethal effects on fish populations may occur well before the lake water pH drops to levels normally considered lethal. If this is the case, failures in fish populations may occur far sooner than would be predicted by changes in lake pH .

Significant Chemical Transformations in Lake Waters

In this section, the elements Carbon, Nitrogen and Sulfur are discussed. Emphasis is placed upon reactions, both chemical and biochemical, which may be important in causing or curing acidification of lakes.

Carbon

(A) Inorganic Carbon

The element most influential in determining the pH of lakes is usually carbon. If a lake water contained no ions other than the CO_2 dissolved from the air, the pH would be about 5.6 (Stumm and Morgan 1970). Such lakes do not exist however, and most contain considerable quantities of dissolved cations such as calcium and sodium, with lower concentrations of anions such as chloride, nitrate and sulfate. The sum of the positive and negative charges must be zero; as there are usually more equivalents of cations than anions*, the balance of negative charge is made up with HCO_3^- or CO_3^{2-} , both of which are potentially volatile.

* excluding the inorganic carbon anions

Alkalinity is defined as the number of equivalents of cations in excess of the number of anionic equivalents, excluding the bicarbonates and carbonates (Stumm and Morgan 1970):

$$\text{eg. Alk} = \text{Ca}^{2+} + \text{Na}^+ + \text{Mg}^{2+} + \dots - \text{Cl}^- \\ - \text{NO}_3^- - \text{SO}_4^{2-} - \dots$$

Thus alkalinity is a measure of the amount of $\text{HCO}_3^- + \text{CO}_3^{2-}$ required to balance the charge in the above equation. If the concentration of all the species on the right side of the equation were reduced by a factor of 2, for example, then the alkalinity, and hence the concentration of $\text{HCO}_3^- + \text{CO}_3^{2-}$, would also be reduced by a factor of 2. As the buffering capacity of a natural water generally depends upon the concentration of $\text{HCO}_3^- + \text{CO}_3^{2-}$, it becomes clear that dilute waters are more poorly buffered than waters of higher ionic strength. In comparing natural waters of the world, Ontario Shield lakes can be said to be among the most dilute (Armstrong and Schindler 1971), and by deduction, among the least buffered. Table 7 compares the major ion composition of two regions of the Ontario Shield with those of world average freshwater.

For the Ontario Shield locations, the ratio of $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ : \text{SO}_4^{2-} + \text{Cl}^- = 2.45$ while the ratio in the world average water is 3.13. This indicates that in addition to being dilute, the Shield water contain a smaller proportion of HCO_3^- than the world average and therefore will be more poorly buffered than would be expected according to ionic

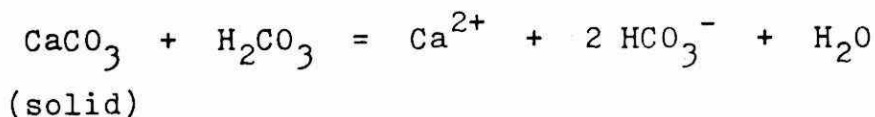
strength. In these lakes it takes very little SO_4^{2-} or NO_3^- anion (from H_2SO_4 or HNO_3) to balance the cations present, and when the balance is struck, the buffering capacity of the HCO_3^- is essentially gone i.e. the alkalinity approaches zero. This explains the rapid pH drop being experienced in many Shield lakes that are subject to mineral acid precipitation (Scheider et al. 1978). After buffering capacity is removed, the H^+ ion concentration is almost directly proportional to the mineral acid input; it is the same as titrating a strong electrolyte solution.

Large natural changes in surface water pH can occur in productive lakes with a wide range of alkalinities (Schindler and Fee 1973 , Wetzel 1975). Diurnal or seasonal fluctuations of 2 - 3 pH units above neutrality are not uncommon due to CO_2 uptake by phytoplankton. Similarly, pH changes can occur in deep lake waters because of increasing CO_2 concentrations produced by biotic respiration. As the bottom waters are often sealed off from the atmosphere by the thermocline, gas exchange with the air cannot take place during stratification and therefore concentrations as high as 2000 $\mu\text{moles L}^{-1}$ of CO_2 have been observed in eutrophic Shield lakes (Schindler et al. 1973). If one assumes an average alkalinity of 130 $\mu\text{equivalents L}^{-1}$ in southern Ontario Shield lakes (Dillon et al. 1978), then the pH of these lakes can be predicted for different concentrations of dissolved inorganic carbon (DIC). According to the diagram given by Deffeyes(1965) the following pH values would approximately obtain:

DIC (uM)	100	500	1000	2000
Predicted pH	7.5	5.8	5.5	5.2

Apparently these Shield lakes could develop quite acid hypolimnia if CO_2 concentrations were above 500 $\mu\text{moles L}^{-1}$. That this acidity would be lethal to some fish seems a moot point however, because a hypolimnion with such high levels of CO_2 would most likely be anoxic and therefore suitable only for bacteria in any case. The acidity is not permanent and will disappear upon lake circulation when the dissolved CO_2 equilibrates with that in the air.

Elevated CO_2 concentrations may have some value in increasing the alkalinities of lake waters. In lakes that receive deliberate additions of CaCO_3 to neutralize anthropogenic acid input, the dissolution of CaCO_3 might be increased by the following reaction (Stumm and Morgan 1970):

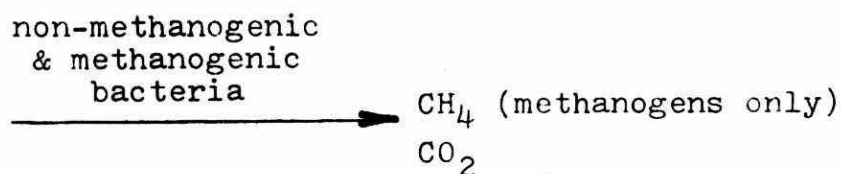
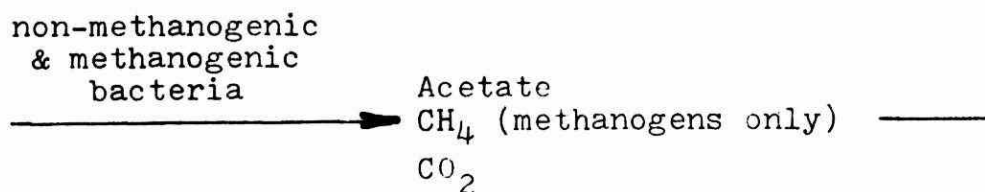
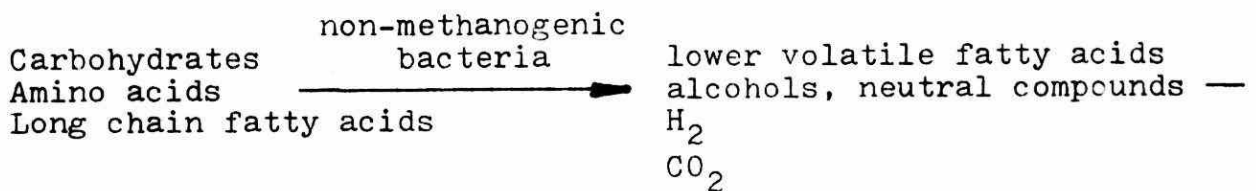


If the CaCO_3 were dumped into the hypolimnion of the basin, it could act as a reservoir of buffer capacity. At times of turnover, the alkaline bottom waters could mix with the surface layers and impart a higher average alkalinity throughout the water column. The possible beneficial effects of eutrophying a lake to increase the bottom water CO_2 , and concurrently adding CaCO_3 (solid) deserves some study. For example, the speed and degree of CaCO_3 dissolution requires

examination because the in situ conditions may significantly alter the kinetics of the reaction.

(B) Methane

Methane can be a major dissolved carbon component in the hypolimnia of productive Shield lakes (Rudd et al. 1976). It is produced in lakes only under highly reducing conditions such as those encountered in sediments. The mode of formation is as follows (Mah et al. 1977):



As can be seen above, the synthesis of CH₄ does not involve the net production or consumption of strong acids or bases and therefore this mechanism would not be predicted to be important in controlling the pH of the water.

Similarly, the bacterial oxidation of CH₄ (Rudd et al. 1976):



should not produce or consume strong acid or base. In the formation and oxidation of methane, the concentration of dissolved CO_2 will change, however, and thereby indirectly affect pH. At present these changes in CO_2 cannot be accurately predicted (J. Rudd-pers. comm.) and therefore the effect of the two processes upon lake water pH is unknown.

(C) Dissolved Organic Carbon

The role of dissolved organic carbon (DOC) in the water chemistry of lakes requires some mention. This carbon pool is often larger than the DIC pool (Schindler unpublished data) in Shield lakes and yet its composition and properties are poorly understood. Humic and fulvic acids are generally acknowledged to be major components of the DOC (Wetzel 1975) but such information is not particularly helpful because these acids are themselves enigmatic. Their roles as complexing agents for trace metals (Chau and Lum-Shue-Chan 1975) and as organic buffers (Oden 1976) have been described only superficially. Several problems that badly need to be resolved are cited here:

When alkalinity measurements are done by titration, in Shield lakes for example, the assumption is usually made that buffering is a function of the $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibria. If these species make up the majority of the weak acids in a lake water, the measurements are probably accurate. However, when the concentrations of these species are low, buffering action of the other weakly dissociable compounds (such as humic acids ?) should be considered. This is particularly true when fixed endpoint alkalinities are performed to the

standard pH 4.5 . Dillon et al.(1978) have stated that buffering capacity of southern Ontario Shield waters is not well estimated by the standard titration technique because critical pH levels of 5 - 5.5 may be attained with the addition of less acid than that predicted by the pH 4.5 alkalinity titrations. The cause of the discrepancy is not clear but it is a significant problem because our estimates about the rate of lake acidification depend upon reliable alkalinity titrations.

In some calculations it is important to account for the majority of dissolved cations and anions present in precipitation or lake water. These ionic balances can be useful in determining basin weathering rates (Schindler et al. 1976) or sources of acidity (Cogbill and Likens 1974). Cation measurements are commonly done by atomic absorption, a method which probably determines most cations present, both bound and not bound. Similarly, anionic measurements, based on wet chemical techniques, are known to overestimate the concentration of some ionic species such as phosphorus (Stainton 1980). If chelation or adsorption of ions onto DOC occurs to a significant degree in natural waters, then the standard chemical determinations may well overestimate the activities of such ions and therefore jeopardize the previously mentioned calculations.

The advent in recent years of the specific ion electrode gives one the capability of measuring activities of ions such as Na^+ , Ca^{2+} , Cl^- , and NH_4^+ , in a procedure that is very similar to that of H^+ ion activity (pH) measurements. It would appear that the electrode determination of ionic

activity might beneficially replace some of the more drastic chemical methods previously used. This would effectively remove the discrepancy between activity and concentration. These direct activity measures should also allow one to determine the 'buffering' capacity of DOC in a fashion similar to that used for alkalinity titrations. Such measurements could help to resolve the total buffering capacity into HCO_3^- and DOC components and perhaps explain the earlier mentioned problems in alkalinity titrations.

Nitrogen

Nitrogen is a major component of protein and therefore is absolutely indispensable in living organisms. In natural waters, nitrogen is usually supplied to the growing organisms as inorganic NO_3^- and NH_3 or as N_2 gas which can be biologically reduced to NH_3 . In Shield lakes the majority of assimilable nitrogen is thought to come from rain and terrestrial runoff, with much lesser amounts from N_2 fixation (Flett et al. 1980).

In this paper, only the possible effects of the nitrogen cycle upon the pH of Shield lakes will be considered.

Chemical budgets for Rawson Lake in the northwestern Ontario Canadian Shield, have shown that about 85 % of the total nitrogen input to the watershed was retained there (Schindler et al. 1976). Only 15 % of the nitrogen passed from the watershed into the lake. Table 8 gives data for the

NW subbasin of Rawson Lake over the years 1970 - 1973.

Of particular interest are the very high retention values for NH_3 and NO_3^- , as well as the apparently zero retention of dissolved organic nitrogen (DON). These data indicate that in watersheds similar to this one, NH_3 and NO_3^- from terrestrial inputs to a lake will be relatively unimportant compared to direct inputs to the lake surface from precipitation. This would apply even if the terrestrial drainage area were 10 times greater in area than the lake.

Brewer and Goldman (1976) have shown that pH and alkalinity changes can occur in sea water when NO_3^- and NH_4^+ are taken up or released by phytoplankton. They give the following set of equations:

- 1) $\text{NO}_3^- \longrightarrow \text{organic N} + \text{OH}^-$ assimilation
- 2) $\text{NH}_4^+ \longrightarrow \text{organic N} + \text{H}^+$ assimilation
- 3) $\text{organic N} \longrightarrow \text{NH}_4^+ + \text{OH}^-$ decomposition
- 4) $\text{NH}_4^+ \longrightarrow \text{NO}_3^- + 2 \text{H}^+$ nitrification
- 5) $\text{NO}_3^- \longrightarrow \text{N}_2 + \text{OH}^-$ denitrification

Precipitation data of Schindler et al. (1976) for northwestern Ontario and those of Likens et al. (1976) for Hubbard Brook, New Hampshire, give the following nitrogen concentrations:

N species uequiv. L^{-1}	NO_3^-	NH_4^+
ELA	18.5	20.9
Hubbard Brook	23.1	12.1
Average	20.8	16.5

The average of the two data sets has been taken and for purposes of simplification, the NH_4^+ and NO_3^- inputs will here be considered to be equal and of 20 uequiv. L^{-1} . If precipitation of 1.0 m a^{-1} is assumed (Pleva 1963), then the annual input would be 20 mequiv. $\text{m}^{-2} \text{ a}^{-1}$ for each ion, if terrestrial input is disregarded.

If complete assimilation of NH_4^+ and NO_3^- occurs, the net change in pH will be zero according to equations 1 and 2. A reasonable next step would be decomposition (equation 3) which would release 40 mequiv. of OH^- and NH_4^+ . In Shield lakes NH_4^+ does not normally accumulate: Scheider et al. (1976) give whole lake average NH_4^+ concentrations in four central Ontario Shield lakes as 2.5 uequiv. L^{-1} , while concentrations in the Experimental Lakes Area (ELA Staff unpublished data) are generally still lower eg. Rawson Lake has about 0.5 uequiv. L^{-1} . To further simplify, the NH_4^+ produced from decomposition is assumed to be completely nitrified with consequent production of 80 mequiv. of H^+ . The overall reaction so far has yielded a net production of 40 mequiv. m^{-2} of excess H^+ ion. Taking 4.14 as the average pH of precipitation in the central Ontario Shield as an example (Dillon et al. 1978) and again assuming 1.0 meter of precipitation (Pleva 1963) the H^+ ion loading would be about 72 mequiv. $\text{m}^{-2} \text{ a}^{-1}$ from precipitation. Thus the production of H^+ ion during N metabolism could conceivably supply a significant fraction of the total acidity to a water body, in this example, about 56 % of that entering from the atmosphere. Certainly these calculations are approximate, but it does appear that nitrogen

metabolism (essentially the oxidation of NH_4^+) can play an important role in the acidification of lakes.

The effect of permanent sedimentation of organic nitrogen has not been mentioned because there are not sufficient data. This process would lower NH_4^+ production and consequently H^+ ion production would drop. Similarly, denitrification (equation 5) has been omitted in this discussion because data concerning its importance are lacking. Chan and Campbell(1980) have shown denitrification to be proceeding at a rate of about $1.1 \text{ mequiv. m}^{-2} \text{ day}^{-1}$ in the epilimnetic sediments of an eutrophic Shield lake and they cite Tiren et al. (1976) as having observed rates of about $5 \text{ mequiv. m}^{-2} \text{ day}^{-1}$. In the first study, denitrification removed only 1.4 % of the $6.29 \text{ g NO}_3^- \text{ N m}^{-2} \text{ a}^{-1}$ entering the lake (Schindler et al. 1973).

Important factors controlling the rate of denitrification appear to be the epilimnetic sediment area as well as NO_3^- concentrations. In addition, pH has been noted to control the process, with optimal values being about 8.0 in laboratory experiments of 20 days duration (Oertli 1972). Chen et al. (1972) observed no nitrification in sediments below pH 5.7 after 14 days incubation in vitro. These results are in contrast with the observed acidification of a Shield lake by the addition of NH_4Cl (Schindler unpublished data) wherein the acidity was probably due to nitrification.

Much more work is required to determine the effects

of NH_4^+ oxidation, net sedimentation and denitrification upon the pH of Shield lakes and further work seems justified in view of their possible significance.

Sulfur

Sulfur appears to be the most important element causing acid precipitation (Dillon et al. 1978 , Likens 1976 , Malmer and Nilsson 1974). The mechanism and rates of sulfuric acid formation by oxidation of SO_2 in the atmosphere have been described by Oden (1976) and Meagher et al. (1978) and therefore discussion here will be limited to the sulfur cycle in water.

A simple unweighted average of the data presented by Armstrong and Schindler (1971) reveals the SO_4^{2-} concentration of Canadian Shield lakes to be about 0.15 mequiv. L^{-1} , very close to the average values observed in the dilute waters of the Experimental Lakes Area and the Haliburton Highlands (0.13 mequiv. L^{-1}). The average Shield HCO_3^- concentration, calculated in this way, is 0.33 mequiv. L^{-1} while in the ELA and Haliburton regions it was only 0.06 mequiv. L^{-1} . Thus it can be seen that in the dilute Shield waters of northwestern and south central Ontario, the HCO_3^- is substantially lower than the average and considerably less than the SO_4^{2-} concentration. Sulfate is already the major anion in these waters.

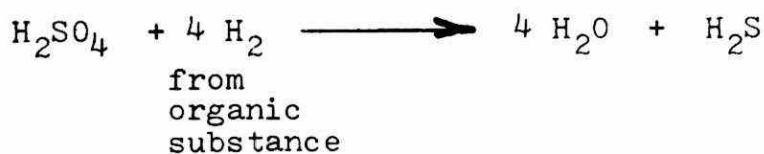
Sulfur is a relatively minor component of living matter, the average being about 0.2 % (Wetzel 1975). If one

assumes 4.0 mg L^{-1} suspended carbon to be a maximum in productive Shield lakes (ELA Staff unpublished data) and that the total organic matter is twice this value, then the average suspended sulfur probably is less than $0.002 * 8 = 0.016 \text{ mg S L}^{-1}$. This represents only $0.5 \text{ uequiv. L}^{-1}$ of the dissolved sulfate pool of $1500 \text{ uequiv. L}^{-1}$ and therefore practically all of the S in the water is in the form of inorganic SO_4^{2-} .

Sulfate reduction is commonly noted to occur in the anoxic hypolimnia of lakes (Wetzel 1975). The reaction is known to be mediated by the bacterial genera Desulfovibrio and Desulfotomaculum in the following way (Kuznetsov et al. 1963):



or



The above is known as dissimilatory sulfate reduction because the SO_4^{2-} is used primarily as a source of oxidant which is used to produce energy for metabolism when organic matter or molecular hydrogen is oxidized. The sulfur itself is not incorporated into the organisms to any degree except as structural matter. The reaction occurs only under strict

anaerobiosis and the absolute limits of their environmental range are pH 4.15 - 9.92 and E_H + 115 to - 450 mv (Bass Becking et al. 1960). According to Ohle (1954) the rate of reaction is proportional to the SO_4^{2-} concentration in the range of 0.4 - 2.7 mequiv. $SO_4^{2-} L^{-1}$ (cited by Wetzel 1975). This concentration range is well above that observed in most Shield lakes (0.15 mequiv. L^{-1}) and thus these bacteria may be sulfate limited in these waters.

A review by Roy and Trudinger (1970) indicates that very little is known about the rate or mechanism of sulfate uptake by these organisms and therefore predictions concerning the disappearance of SO_4^{2-} from lakes are not easily made. It may be possible, however, to gain some information about the rate of sulfate consumption by examining changes in SO_4^{2-} and H_2S concentrations in lakes as a function of time, and relating these rates to the supply of organic matter. Such data are probably already available for a number of lakes.

The fact that SO_4^{2-} reduction can significantly increase the alkalinity of a Shield lake has been shown by Schindler et al. (1980). In one year they found that as much as 11 uequiv. L^{-1} of alkalinity was supplied in this way. Equally interesting was the observation that the H_2S produced was nearly completely held in the sediments, probably as an iron sulfide. No appreciable return of H_2S occurred at lake turnover and therefore the increase in alkalinity was permanent because H_2S was not reoxidized to H_2SO_4 .

The process of assimilatory sulfate reduction might also impart alkalinity to a lake water:



This reaction is common to many organisms (Roy and Trudinger 1970). If organic production were at a high rate in a water body, it is possible that enough sulfate would be assimilated and subsequently released (as H_2S in sediments and hypolimnetic waters) to decrease the sulfate concentration, and hence the acidity in the water. To cause more than just a seasonal decrease in acidity, the H_2S would have to be permanently bound in the sediments as was noted in the dissimilatory reduction of Schindler et al. (1980).

Both of these sulfur reduction processes show promise as possible means of combatting the acidification of lakes and thus they deserve further study. Obvious questions which require answers are: 1) What is the relationship between rate of sulfate reduction and organic substrate concentration ? 2) What is the relationship between the rate of sulfate reduction and sulfate concentration ? 3) At what acid pH will the reduction halt ? 4) Would eutrophication by nutrient addition increase the rate of reduction ? 5) Would eutrophication be more detrimental than the acidity being fought ?

Some enzymes involved in sulfate reduction are known to be sensitive to chromate, tungstate and selenate (Roy and Trudinger 1970) and it is possible that dissolved heavy

metals will affect the sulfate reducing bacteria at some concentration. As heavy metals are known to occur in acid precipitation (Schofield 1972) and as leaching of heavy metals can occur from the sediments of acidified lakes (Schindler et al. 1980), the effects of heavy metals upon the sulfate reduction process deserve some attention. This will be especially true if sulfate reduction shows promise as a remedial measure to counter acidification.

Conclusions

The input of anthropogenic acid, via precipitation, will probably increase the rate at which soil buffering reactions occur and therefore the finite quantity of buffer in the soils will be more rapidly consumed. An estimate of how much faster the buffer consumption will be, under the influence of anthropogenic acids, is not presently possible. To make this estimate it is necessary to know how fast the buffering agents are being naturally consumed. As yet, this information is unavailable. In short, if the production of natural soil acids is high relative to the anthropogenic input, then the soils should be little affected by the additional man-made acid. As a result, the soils should continue to neutralize incoming acids long into the future. If, however, the rate of natural soil production is relatively low, then the additional acid input may greatly accelerate the consumption of soil buffering material.

Considering only the worst case, wherein soil buffering capacity is being rapidly consumed, there are two possible results at least:

- 1) If the major buffering is due to calcium or magnesium carbonates, then it is possible that the soil would be completely depleted of these bases, even in the C horizon. This would be especially true in Shield soils which were initially poor in bases. Once depleted, the soils would no longer neutralize the incoming acid and both the soil and the

drainage water from it would be as acid as the precipitation. Lakes receiving drainage from such soils would likely be of an acidity similar to that of the precipitation.

2) If the major buffering is due to reactions with minerals such as plagioclase, then the period over which buffering capacity might exist would depend upon the quantity of reactive minerals in the soils. Some Shield soils do contain large amounts of plagioclase (Brunskill et al. 1971) and in these soils one would expect the buffering capacity to persist over a very long time. A watershed composed of such soils would tend to maintain the pH of a lake above the pH of the precipitation.

As the till of south central Ontario is of variable thickness and commonly less than 1.0 meter in depth, it is likely that buffering will often be incomplete and therefore it is expected that mineral acid runoff will occur from the terrestrial watershed. Dissolved aluminum would be expected in runoff with a pH of less than about 5.

The Shield stream waters in springtime can be predicted to become more acid with increasingly acid precipitation. The acid streams may be the most serious immediate problem because mortality of larvae from spring spawning fish could now be in an elevated state and yet be undetected.

Acid streams are a further problem because they are not easily neutralized. Lining a streambed with crushed limestone (CaCO_3) does not appear to be feasible because the dissolution of the material is too slow to be beneficial as a buffer. An experiment outlined by Kuznetsov (1963) showed that a channel containing acid minewater in contact with 5 tonnes of finely crushed limestone was only 50 % neutralized in one hour. This length of contact time would not likely be experienced by a running stream. It would seem that more soluble (and probably more expensive) buffering material will have to be tested for this purpose. An obvious alternative to neutralizing the streams is the regular stocking of lakes with these sensitive species, but in less acidic periods of the year.

The benefit of adding CaCO_3 as a buffer in acidic Shield lakes has already been demonstrated (Scheider and Dillon 1976) and further studies concerning its use appear justified. The type of limestone can have considerable bearing upon its rate of dissolution (Morgan and Salter 1923) and thus some practical testing of available materials is warranted.

Deposition of buffering mineral into hypolimnetic waters containing elevated concentrations of CO_2 may be a means of ensuring dissolution of the mineral. The CO_2 rich waters should enhance dissolution but the reaction kinetics need studying. If the mineral were crushed to an appropriate size, the dissolution time could be slow enough to ensure a continued buffering effect over a period of years. In non-

productive bodies of water, where hypolimnetic CO_2 concentrations were low, fertilization of the lake might be helpful in dissolving the mineral buffer by increasing the bottom water CO_2 . Hypotheses such as the above require testing, and given the abundant supply of acids in some regions, there probably is no deficiency of lakes in which to test them. The gravity of the acidification problem in south central Ontario would seem to preclude long term laboratory experimentation which may or may not evaluate the hypotheses. Whole lake experiments appear preferable because the results are more easily applied to other lakes (Johnson and Vallentyne 1971).

For information concerning the effects of nitrogen inputs upon the pH of lakes, there are already considerable data available for at least one Shield lake (ELA Staff unpublished data). Although the experimental manipulation of this lake (No. 304) was directed toward understanding eutrophication, many of the results should be directly applicable in illustrating the effects of various nitrogen species upon lake pH. These data definitely deserve examination.

Conclusions about the role of sulfate reduction as a buffering mechanism in Shield lakes are premature (Schindler et al. 1980) but results are encouraging and merit further research. A number of questions to be addressed have been previously identified in this paper.

Finally, the technology of ionic species measurement

is due for a review. In some cases the specific ion electrode may give better information about ion activities than do the 'classical' techniques. As H^+ ion is at the center of this type of research, close attention to the practical determination of pH is critical (Galloway et al. 1979).

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FIGURE CAPTIONS

- Figure 1 Typical podzol profile (taken from Strahler and Strahler 1973, Fig. 12.15).
- Figure 2 Depth to carbonates in soil profiles versus annual rainfall along the 11 C annual isotherm in central United States (from Black 1968, Fig. 5.10)
- Figure 3 pH and titratable H^+ ion concentration in surface soils versus annual rainfall along the 11 C annual isotherm in central United States (from Black 1968, Fig. 5.10).
- Figure 4 (a) Exchangeable aluminum at different pH values and (b) Exchangeable aluminum as a percentage of of the principal exchangeable ions at different pH values in soils of North Carolina (from Black 1968, Fig. 5.4)
- Figure 5 Solubility of aluminum in water, and concentration of aluminum in displaced soil solutions at different pH values (from Black 1968, Fig. 5.13).
- Figure 6 Incongruent dissolution of kaolinite: (a) solubility of gibbsite (b) hypothetical (component) solubility of kaolinite for H_4SiO_4 concentration = $10^{-2.7}$ M. (from Stumm and Morgan 1970, Fig. 8-4).

FIGURE 1

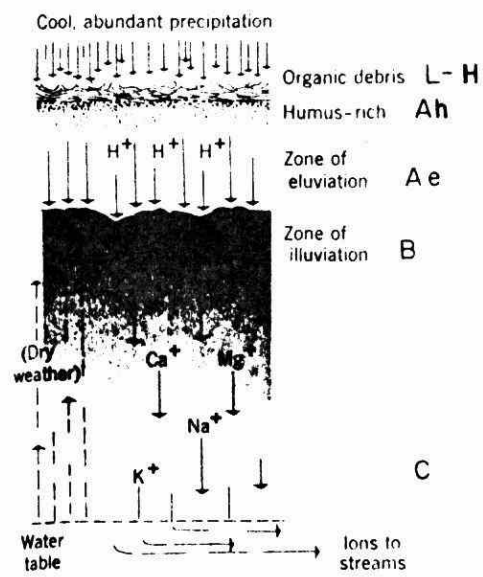


FIGURE 2

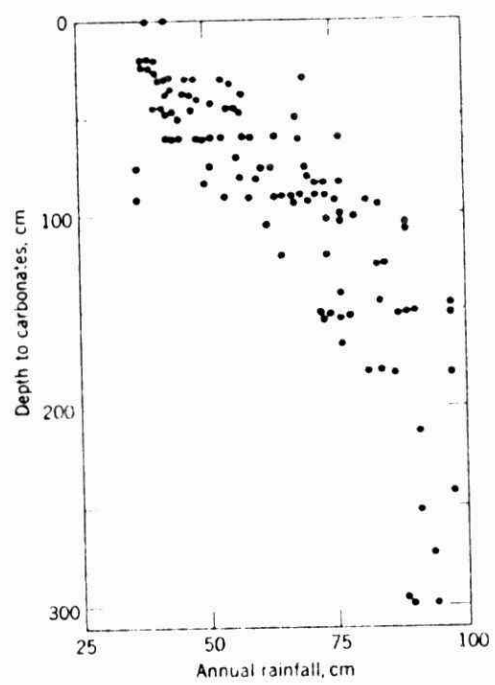
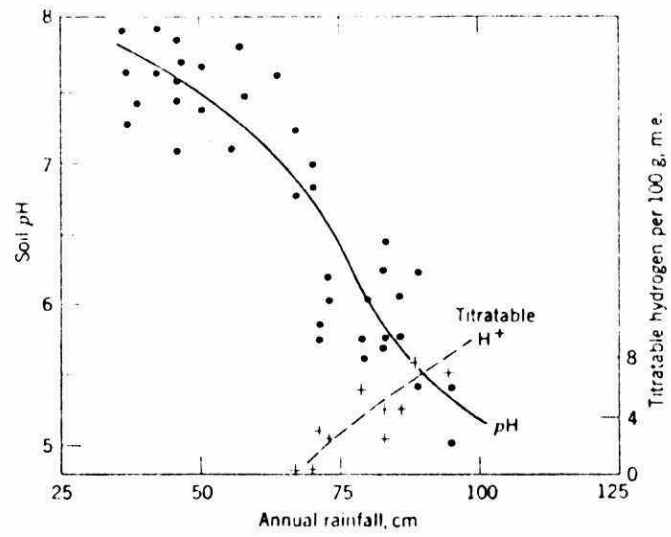


FIGURE 3



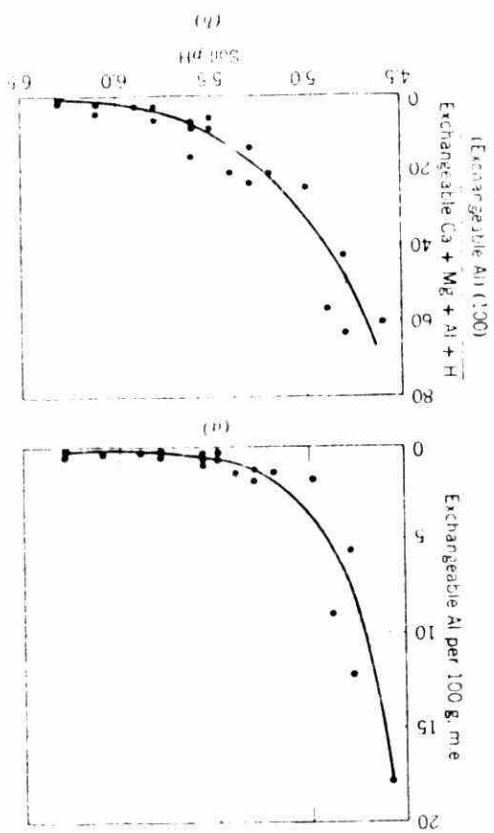


FIGURE 4

FIGURE 5

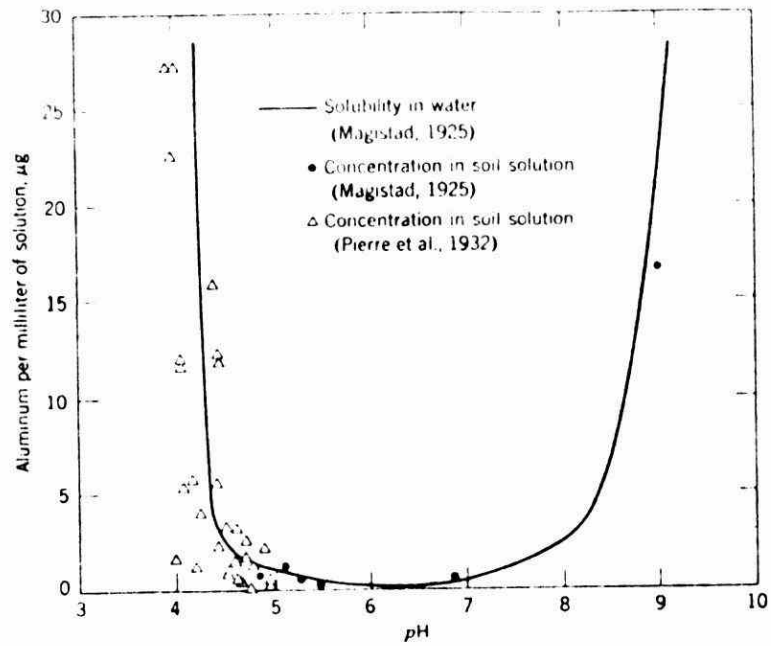


FIGURE 6

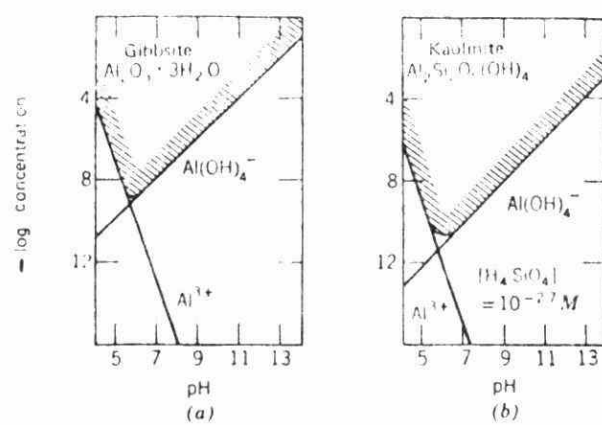


TABLE CAPTIONS

- Table 1 Mean concentration and standard deviation of ionic constituents in Hubbard Brook, New Hampshire rainfall during 1963 - 1974 (from Likens et al. 1976)
- Table 2 Partial composition of precipitation, throughfall and stemflow in a northern Ontario Jack Pine forest (from Foster 1974).
- Table 3 Partial composition of precipitation and throughfall in a hardwood forest, Hubbard Brook, New Hampshire (from Eaton et al. 1973).
- Table 4 Relationship between the net amount of each component removed from the summer canopy via throughfall plus stemflow and total standing crop of each component in the leaves during July. Data for hardwood forest in Hubbard Brook, New Hampshire (from Eaton et al. 1973).
- Table 5 Profile showing physical and chemical characteristics of a Humo - Ferric podzol: A) General description
B) Chemical composition (from Clayton et al. 1977).
- Table 6 Soil pH values at different depths in a control plot and a plot treated with ammonium sulfate equivalent to 840 Kg ha^{-1} (from Black 1968).
- Table 7 Comparison of some dissolved components in Shield and world average freshwaters (data calculated from Armstrong and Schindler 1971, Table 10).

Table 8 Relationship of nitrogen compounds in runoff and precipitation in the NW subbasin of Rawson Lake watershed for 1970 - 1973 (data calculated from Schindler et al. 1976 and ELA unpublished data).

TABLE 1

Ion	Mean Concentration u eq. L ⁻¹	S.D. of Mean u eq. L ⁻¹
Ca ²⁺	8.6	1.1
Mg ²⁺	3.7	0.7
K ⁺	1.9	0.5
Na ⁺	5.4	0.6
NH ₄ ⁺	12.1	0.7
H ⁺	73.3	3.0
SO ₄ ²⁻	59.7	2.4
NO ₃ ⁻	23.1	1.7
Cl ⁻	14.4	2.5
PO ₄ ³⁻	0.25	-

Sum Anions = 105.0 -/+ 3.4 u eq. L⁻¹

Sum Cations = 97.5 -/+ 3.9 u eq. L⁻¹

TABLE 2

	Total N	NO ₃ ⁻ N	P	K	Ca	Mg	H ⁺	pH
	mg L ⁻¹	u eq. L ⁻¹						
Precipitation	0.59	26.4	0.4	12.8	17.2	5.4	11.8	4.93
Throughfall	0.59	13.6	0.6	47.6	26.7	9.1	24.6	4.61
Stemflow	0.74	2.1	2.4	268.3	108.0	70.3	155.0	3.81

TABLE 3

Component Name	Precipitation u eq. L ⁻¹	Average Throughfall u eq. L ⁻¹
Ca ²⁺	8	72
Mg ²⁺	2.5	37
K ⁺	1.8	130.7
Na ⁺	2.6	5.7
NO ₃ ⁻	15.7	42.7
NH ₄ ⁺	15.0	67.2
Org. N	-	-
PO ₄ ³⁻	-	36.8
SO ₄ ²⁻	55.1	294.8
Cl ⁻	12.7	35.3
H ⁺	87.	10.7
Sum cations	116.9	323.3
Sum anions	83.4	372.8

TABLE 4

Component Name	Net Throughfall and Stemflow Kg/ha	Standing Crop (leaves) Kg/ha	Ratio
Na	0.31	0.057	5.61
S	20.98	5.72	3.67
K	30.08	33.32	0.90
Mg	2.00	3.98	0.50
Ca	6.73	22.24	0.30
N	9.90	77.17	0.13
P	0.68	6.00	0.11
Org. Matter	115.44	3207.6	0.04

TABLE 5

A

ORTHIC HUMO-FERRIC PODZOL

HOLMESVILLE SERIES

Location:	Gillespie settlement — 4 miles S of Grand Falls, N.B. 47° N 67°40' W
Physiography:	Undulating ground moraine
Drainage:	Well drained
Parent material:	Gravelly moderately coarse (sandy loam) till
Vegetation:	Mixed forest, balsam, maple, birch, and shrubs
Climate:	Boreal cool, perhumid

Horizon	Depth cm (in.)	
L-H	10-0 (4-0)	Moderately and well-decomposed litter of needles and twigs.
Ae	0-13 (0-5)	Pinkish gray (5YR 6.5/1 m, 8/1 d) silt loam; very weak, medium platy; very friable; plentiful roots; abrupt, irregular boundary; intermittent evidence of tree-throws; extremely acid.
Bfh	13-38 (5-15)	Yellowish red to strong brown (5YR to 7.5YR 5/6 m, 8.5YR 6/5 d) silt loam; moderate, medium granular; very friable; plentiful to few roots; abrupt, wavy boundary; very strongly acid.
Bf	38-84 (15-33)	Light olive brown (2.5Y 5/5 m, 10YR 7/4 d) sandy loam; weak, fine granular; very friable; plentiful to few roots; abrupt, smooth boundary; medium acid.
BC	84-180 (33-71)	Light olive brown (2.5Y 5/3 m, 6/2 d) sandy loam; very weak, fine granular to amorphous; friable; few roots; some pebbles; clear smooth boundary.
C	180-206 (71-81)	Dark grayish brown (2.5Y 4.5/2 m, 6.5/2 d) gravelly sandy loam; pseudoplaty; slightly firm and compact; medium acid.

SOIL TYPE:

ORTHIC HUMO-FERRIC PODZOL

HOLMESVILLE SERIES

Depth cm	Horizon	Particle size				Dithionite		Oxalate		pH
		Sand	Clay	Fine clay	OM	Fe	Al	Fe	Al	CaCl ₂
		3A1b	3A1b	3A1b	6A1a	6C3	6G5	6C5	6G6	8B1d
		%	%	%	%	%	%	%	%	
0- 13	Ae	24.7	8.5	6.5	1.88	0.18	0.16	0.05	0.15	3.3
13- 38	Bfh	31.4	16.8	12.7	7.26	3.26	1.40	2.60	1.38	4.3
38- 84	Bf	55.4	7.8	5.6	2.13	1.22	0.79	0.56	1.01	4.9
84-180	BC									
180-206	C	59.0	9.9	3.5	0.22	0.56	0.38	0.18	0.18	5.1
Cation exchange										
Depth cm	Horizon	Ca + Mg	Al	Capacity	Base sat	Capacity	Acetate Base sat.			
		5A3b	5A3b	5A3b	5A3b	5A6	5A6			
		meq/100 g			%	meq/100 g	%			
0- 13	Ae	1.7	5.7	7.4	23	14.7	12			
13- 38	Bfh	1.5	4.1	5.6	27	28.0	5			
38- 84	Bf	0.6	0.9	1.5	40	9.8	6			
84-180	BC									
180-206	C	0.5	0.1	0.6	83	4.6	11			

TABLE 5

TABLE 6

Depth of Sampling cm	Soil pH	
	Control Plot	Ammonium Sulfate Plot
0 - 15	5.5	4.9
15 - 30	5.5	5.0
30 - 46	5.4	5.0
46 - 61	5.5	5.4

TABLE 7

Location	m equivalents L ⁻¹						
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻
ELA	.08	.074	.039	.010	.063	.039	.062
Haliburton Highlands	.095	.107	.030	.008	.081	.017	.067
World Average	.750	.337	.274	.059	.233	.220	.957

ELA - northwestern Ontario

Haliburton Highlands - south central Ontario

TABLE 8

Nitrogen Species	Precipitation			Runoff		<u>Runoff X 100</u> Precip. (%)
	Mass Kg	Conc'n. ug L ⁻¹ (Avg)	% of Total	Mass Kg	% of Total	
* NH ₄ ⁺	147.9	.293	37.3	4.92	8.5	3.3
* NO ₃ ⁻	130.8	.259	33.0	2.87	5.0	2.2
* TDN	324.1	.642	81.7	50.3	86.8	15.5
* Susp N	72.7	.144	18.3	7.68	13.3	10.6
DON	45.4	.090	11.5	45.4	78.3	100.
Total N	396.8	.786	100.	57.98	100.	14.6

Total N = TDN + Susp N

DON = TDN - (NH₄⁺ + NO₃⁻)

* indicates independent measurements

All data from Schindler et al. (1976) and ELA Staff unpublished data.

1867
434
90
1955
TD